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THE EFFECT OF THE FINELY DISPERSED COMPONENT ON THE FORMATION OF A POROUS PERMEABLE STRUCTURE IN CERAMICS

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The effect of the clay component on the molding of a permeable ceramic structure is studied, and the possibility of using clays from the Tula Region as a binder for permeable ceramics is demonstrated.

Clay is the traditional binding agent in ceramics technology. It ensures not only the molding and the conservation of the shape of a molded article, but also its sintering, usually at relatively low temperatures. The use of clay in the production of porous permeable ceramics for different purposes was frequently discussed in the literature. The binders are usually high-quality plastic kaolinite clays, such as Veselovskoe, Novoraiskoe, etc. It was observed that the clay component has a negative effect on the formation of a porous ceramic structure and it is recommended to use the minimum quantities of binding clay [1]. At the same time, many deposits of white-burning clays that are mostly located in Ukraine are little accessible to a Russian manufacturer, primarily due to the high cost of these clays. Therefore, it is essential to develop the domestic material resources.

The purpose of the present paper is to solve a complex problem: to study the effect of the argillaceous component on the formation of a permeable structure in ceramic materials and evaluate the possibility and expediency of using clay from the Kimovskoe and the Novomoskovskoe deposits (Tula Region) as a binder for permeable ceramics.

The object of analysis was alumina-based ceramics for electrolysis membranes [2]. Alumina G00 is a polyfractional filler (particle size of $2 - 100$ μm) without too dense a particle packing, which has a favorable effect on the permeability of ceramics. The properties of alumina – clay two-component systems and alumina – clay – ash three-component systems were investigated. The considered range of compositions is shown in Fig. 1.

The Novomoskovskoe clay belongs to low-melting medium-plasticity clay with a refractoriness below 1350°C and a high content of free quartz. The Kimovskoe clay is a schistose material with a refractoriness of 1620°C, a low free quartz content, and a high calcination loss (Table 1). The clay content varied within sufficiently wide limits: from 10 to 40 vol.%, which made it possible to estimate the effect of the clay components on the formation of a porous ceramic structure.

The study of the sintering process in clays indicated that the clays do not reach the sintered state, have a narrow sintered-state interval (not more than 50°C) and at a temperature of 1200°C and over become swelled (the Kimovskoe clay) or fused (Novomoskovskoe clay). Therefore, the
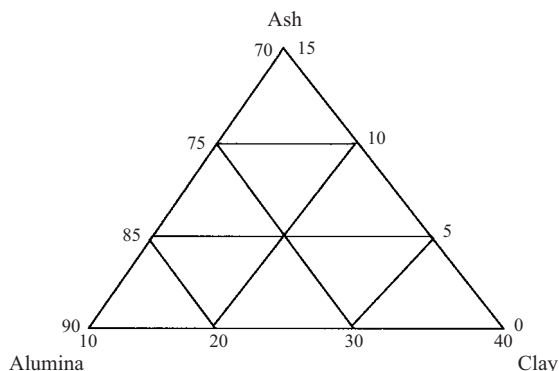
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Fig. 1. Considered components of alumina – clay – ash system.

TABLE 1

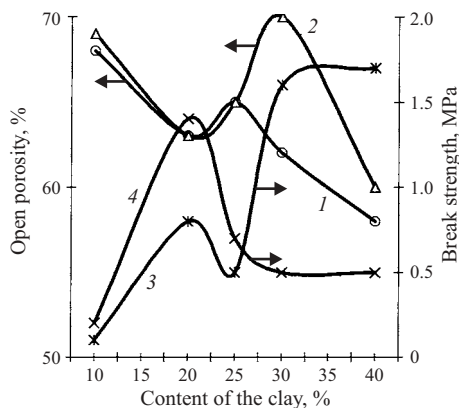| Clay deposit	Weight content, %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	calcination loss	free SiO_2
Novomoskovskoe	78.3	11.5	1.76	1.92	0.60	3.61	51.2
Kimovskoe	45.1	28.8	0.85	1.24	0.92	21.1	7.1

Fig. 2. Dependence of open porosity (*1*, *2*) and breaking strength (*3*, *4*) of samples on the content of the Novomoskovskoe (*1*, *3*) and the Kimovskoe clay (*2*, *4*).
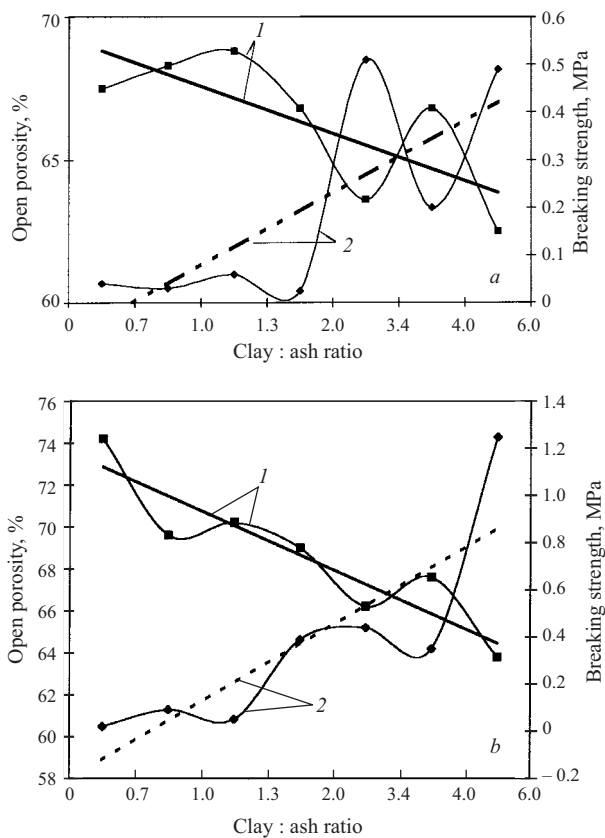

Fig. 3. Dependence of open porosity (*1*) and breaking strength (*2*) on the clay : ash ratio for materials based on the Kimovskoe clay (*a*) with a correlation coefficient of 0.98 (*1*) and 0.90 (*2*) and based on the Novomoskovskoe clay (*b*) with a correlation coefficient of 0.85 (*1*) and 0.84 (*2*).

TABLE 2

Component of ceramic material*	Volume content, %	Open porosity, %	Gas permeability coefficient, μm^2	Mean permeability diameter of pores, μm	Breaking strength, MPa
Alumina	90	68.4	0.006	0.5	0.16
Clay 1	10				
Alumina	90	68.0	0.007	0.6	0.06
Clay 2	10				
Alumina	80	62.7	0.003	0.3	1.42
Clay 1	20				
Alumina	80	63.0	0.003	0.4	0.78
Clay 2	20				
Alumina	60	60.0	0.005	0.4	0.52
Clay 1	40				
Alumina	60	57.8	0.005	0.5	1.63
Clay 2	40				
Clay 1	10	69.0	0.004	0.3	0.16
Ash	5				
Clay 1	20	67.6	0.009	0.6	0.35
Ash	5				
Clay 2	10	66.8	0.028	0.7	0.02
Ash	5				
Clay 2	20	66.8	0.015	0.9	0.20
Ash	5				

* Clay 1: Novomoskovskoe deposit; clay 2: Kimovskoe deposit.

and gas permeability coefficient (Table 2). It is established that an introduction of 10 vol.% clay does not ensure the sintering of ceramics materials (breaking strength below 1 MPa, open porosity 68.0 – 68.5%, water absorption 57.9 – 63.9%). As the quantity of clay grows, the values of open porosity decrease, and the strength and density of the material increase. In using the Novomoskovskoe clay, these processes are more perceptible (Fig. 2), whereas the samples made of the Kimovskoe clay exhibit fraction growth of the porosity and, accordingly, decreased strength (with the volume content of clay exceeding 25%). This is probably due to the high content of hymus impurities in the specified clay (around 20 vol. %), which burn out and ensure additional increase in the porosity.

At the same time, one should take into account that the Novomoskovskoe clay contains over 50 vol.%. free quartz, whose polymorphous transformations also may cause modification of the formation of a porous structure in ceramic materials. These processes presumably facilitate a sharp increase in the gas permeability coefficient against the background of a less significant increase in the mean hydraulic size of the pores and insignificantly varying porosity (Table 2) and yield high values of the mean hydraulic size of pores and a wide interval of their size distribution. Elongated and rather large crack-like pores are formed, which agrees with the earlier published data [3]. One can suppose that the insignificant fluctuation of the gas permeability coefficient and the pore size against the background of a growing density of materials with an increasing content of the clay binder contribute to a

ceramic materials were fired at a temperature of 1150°C, at which the highest breaking strength is registered (7 – 11 MPa) with an open porosity of 16 – 18%.

In spite of the different chemicomineralogical compositions, both clays have similar values of strength, porosity,

decreased content of the sealed and opened porosity, whereas the effective porosity level is preserved.

It should be noted that the introduction of burning-out additives (ash) into a system with a low clay content (less than 20 vol.%) has a weak effect on the porous structure parameters. Thus, the values of porosity and density vary insignificantly. The character of the dependence of properties is predictable: as the content of the burning-out additive grows, the gas permeability increases due to an increased pore size, and the strength sharply decreases. It can be assumed that the mainly slot-like porous structure of the alumina – clay materials does not undergo qualitative modifications on introducing 5 – 15 vol.% burning-out additives. Thus, quantitative processes proceed in the porous structure mainly due to additional loosening of the structure by the product of ash combustion and the redox reactions [3].

As the clay content grows, the effect of the burning-out additive is manifested more clearly, since an increasing content of the clay component decreases the effective pore shape that is formed due to packing of narrowly fractionated alumina grains and, apparently, due to a modification of the type of the pore structure.

With an increasing burning-out additive, the relative part of the finely dispersed component increases and, accordingly, the relative content of the filler decreases. It was observed that the properties of ceramics depend not so much on a varying content of a particular component as on the ratio of the components. A virtually linear dependence of the density,

water absorption, and porosity of the material on the clay : ash ratio is registered. As this ratio increases, the density grows and the water absorption and porosity decrease (Fig. 3).

Thus, the use of clay from the Tula Region as a temporary technological binder in mixtures for permeable porous ceramics based on a polyfractional filler even in the amount of 40 vol.% ensures minimum values of open porosity of at least 50% with a mean hydraulic pore size of 0.3 – 1.5 μm. The increased clay content in this case not only increases the strength of the ceramics several times, but also facilitates the formation of a permeable porous structure. Due to the specifics of their chemicomineralogical composition, the considered clays of the Tula region can be considered promising for use in the technology of porous permeable ceramics, as their use makes superfluous an additional introduction of burning-out additives that have a negative effect on the strength properties of ceramics.

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